



The following Communications have been judged by at least two referees to be “very important papers” and will be published online at www.angewandte.org soon:

A. Patzer, M. Schütz, T. Möller, O. Dopfer*

Infrared Spectrum and Structure of the Adamantane Cation: Direct Evidence for Jahn–Teller Distortion

C. Lux, M. Wollenhaupt, T. Bolze, Q. Liang, J. Köhler, C. Sarpe, T. Baumert*

Circular Dichroism in the Photoelectron Angular Distributions of Camphor and Fenchone from Multiphoton Ionization with Femtosecond Laser Pulses

J. Lu, C. Aydin, N. D. Browning, B. C. Gates*

Imaging Isolated Gold Atom Catalytic Sites in Zeolite NaY

F. Liao, Z. Zeng, C. Eley, Q. Lu, X. Hong,* S. C. E. Tsang*

Electronic Modulation of a Copper/Zinc Oxide Catalyst by a Heterojunction for Selective Hydrogenation of Carbon Dioxide to Methanol

H. T. Baytekin, B. Baytekin, J. T. Incorvati, B. A. Grzybowski*
Material Transfer and Polarity Reversal in Contact Charging

N. Metanis, D. Hilvert*

Strategic Use of Non-native Diselenide Bridges to Steer Oxidative Protein Folding

M. Mastalerz,* I. M. Oppel

Rational Construction of an Extrinsic Porous Molecular Crystal with an Extraordinary High Specific Surface Area

S. C. S. Lai, A. N. Patel, K. McKelvey, P. R. Unwin*

Definitive Evidence for Fast Electron Transfer at Pristine Basal Plane Graphite from High-Resolution Electrochemical Imaging



“What I appreciate most about my friends is loyalty and frankness.

The greatest scientific advance of the last decade was published at the very beginning of the 21st century: the first draft sequence and analysis of the human genome ...”

This and more about Max Malacria can be found on page 4518.

Author Profile

Max Malacria — 4518–4519



A. Simon



S. Herres-Pawlis



M. Grätzel

News

Terrae Rarae Prize: A. Simon
NRW-Innovation Prize: S. Herres-Pawlis
Albert Einstein World Award of Science:
Michael Grätzel — 4520

Richard Bader (1931–2012)

Obituaries

P. W. Ayers, G. Frenking* — 4521–4522

Beyond the Finite

Roald Hoffmann, Iain Boyd Whyte

Books

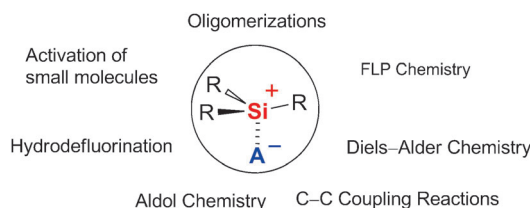
reviewed by J. M. Thomas — 4523

Highlights

Silylium Ions

A. Schulz,* A. Villinger — 4526–4528

“Tamed” Silylium Ions: Versatile in Catalysis



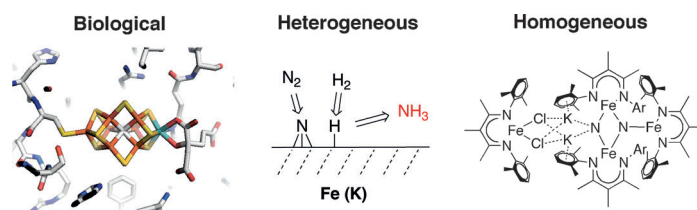
Cations for all seasons: Silylium cations, because of their high Lewis acidity, are suitable for catalysis like almost no other class of reactive cations. Starting from

a new, elegant synthetic route to triarylsilylium ions and their application in hydrogen activation, the general potential of silylium ions in synthesis is discussed.

Nitrogen Fixation

M. G. Scheibel,
S. Schneider* — 4529–4531

New Insights into the Biological and Synthetic Fixation of Nitrogen



The fixation with fixation: Microorganisms have converted atmospheric nitrogen into ammonia for millions of years under ambient conditions, whereas the Haber–Bosch process requires high pressures and temperatures. Some recent

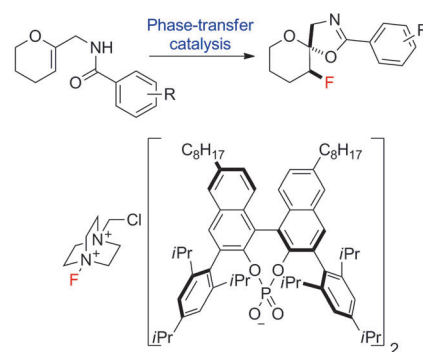
studies on the biological and synthetic generation of ammonia should contribute to a better understanding of the mechanism of this reaction, which remains one of the most challenging goals for catalysis.

Asymmetric Fluorination

U. Hennecke* — 4532–4534

A New Approach towards the Asymmetric Fluorination of Alkenes Using Anionic Phase-Transfer Catalysts

Chiral anions can do it: Asymmetric phase-transfer catalysis is no longer limited to cationic catalysts. Lipophilic BINOL phosphate anions are superior catalysts for the asymmetric electrophilic fluorination of alkenes under phase-transfer conditions (see picture). Now complex fluorinated compounds can be synthesized selectively from simple alkene starting materials.

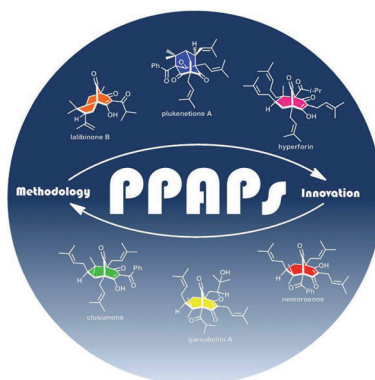


For the USA and Canada: ANGEWANDTE CHEMIE International Edition (ISSN 1433-7851) is published weekly by Wiley-VCH, PO Box 191161, 69451 Weinheim, Germany. Air freight and mailing in the USA by Publications Expediting Inc., 200 Meacham Ave., Elmont, NY 11003. Periodicals

postage paid at Jamaica, NY 11431. US POSTMASTER: send address changes to *Angewandte Chemie*, Journal Customer Services, John Wiley & Sons Inc., 350 Main St., Malden, MA 02148-5020. Annual subscription price for institutions: US\$ 11,738/10,206 (valid for print and electronic / print or electronic delivery); for

individuals who are personal members of a national chemical society prices are available on request. Postage and handling charges included. All prices are subject to local VAT/sales tax.

Recently completed total syntheses and the ingenious synthetic approaches developed for the construction of the biologically significant polycyclic polyprenylated acylphloroglucinols (PPAPs) are presented in this Review. The state-of-the-art synthetic methods and strategies, current limitations, as well as the outlook for this field are highlighted.

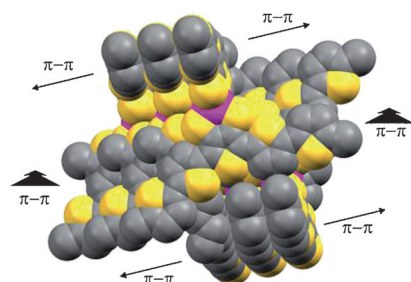


Reviews

Natural Product Synthesis

J.-A. Richard, R. H. Pouwer,
D. Y.-K. Chen* _____ **4536–4561**

The Chemistry of the Polycyclic
Polyprenylated Acylphloroglucinols



X marks the spot! A fascinating packing motif is observed in a novel cruciform oligothiophene containing a Ge (violet; see picture) spiro center. Long-range interchain interactions between molecules and strong electronic coherence between orthogonal chains within the molecules are present. Such ordering is advantageous for bulk charge transport, as demonstrated by high short-circuit currents in bulk heterojunction organic solar cells.

Communications

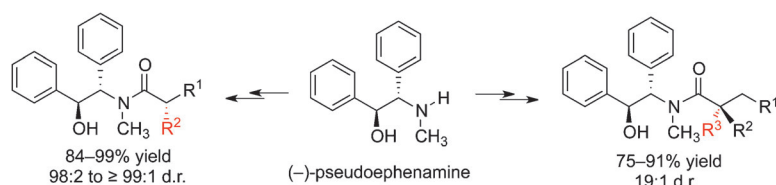
Stacking Interactions

I. A. Wright, A. L. Kanibolotsky,
J. Cameron, T. Tuttle, P. J. Skabara,*
S. J. Coles, C. T. Howells,
S. A. J. Thomson, S. Gambino,
I. D. W. Samuel* _____ **4562–4567**

Oligothiophene Cruciform with
a Germanium Spiro Center: A Promising
Material for Organic Photovoltaics



Frontispiece



Unrestricted: Pseudoephedrine is introduced as a versatile chiral auxiliary and an alternative to pseudoephedrine in asymmetric synthesis. It is free from regulatory restrictions and leads to remarkable stereocontrol in alkylation

reactions, especially in those that form quaternary carbon centers. Amides derived from pseudoephedrine exhibit a high propensity to be crystalline substances, and provide sharp, well-defined signals in NMR spectra.

Synthetic Methods

M. R. Morales, K. T. Mellem,
A. G. Myers* _____ **4568–4571**

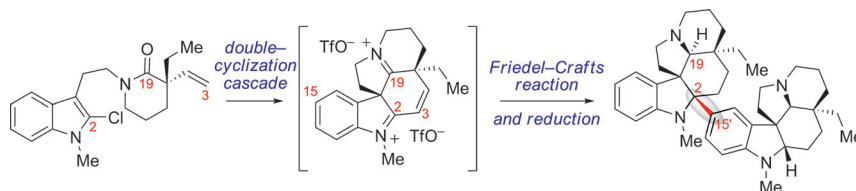
Pseudoephedrine: A Practical Chiral
Auxiliary for Asymmetric Synthesis



VIP Alkaloid Synthesis

J. W. Medley,
M. Movassaghi* — 4572–4576

A Concise and Versatile Double-Cyclization Strategy for the Highly Stereoselective Synthesis and Arylative Dimerization of Aspidosperma Alkaloids



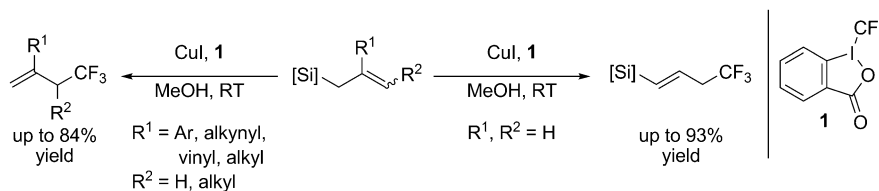
Building cycles: A strategy for the concise, stereoselective synthesis of aspidosperma alkaloids and related structures via a common putative diiminium ion intermediate is reported. The approach enables the dimerization of aspidosperma-

type structures at the sterically hindered C2 position. The intermediate is prepared in one step from the shown lactam through an electrophilic double-cyclization cascade (see scheme; Tf = trifluoromethanesulfonyl).

C–CF₃ Bond Formation

R. Shimizu, H. Egami, Y. Hamashima,
M. Sodeoka* — 4577–4580

Copper-Catalyzed Trifluoromethylation of Allylsilanes



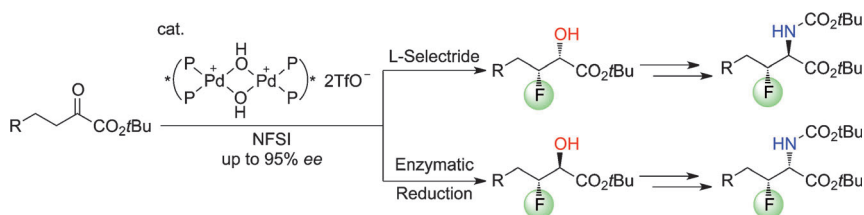
CF₃ on C_{sp³}: Trifluoromethylation of allylsilane derivatives was accomplished through the use of CuI and Togni's reagent (**1**) under mild conditions. The reaction of allylsilanes without a substituent

in the 2-position gave vinylsilane derivatives, while 2-substituted allylsilanes afforded desilylated products. The utility of the products was demonstrated through their further transformation.

Organofluorine Chemistry

S. Suzuki, Y. Kitamura, S. Lectard,
Y. Hamashima,
M. Sodeoka* — 4581–4585

Catalytic Asymmetric Mono-Fluorination of α -Keto Esters: Synthesis of Optically Active β -Fluoro- α -Hydroxy and β -Fluoro- α -Amino Acid Derivatives



Enantioselective mono-fluorination of α -keto esters was achieved using a mildly basic palladium μ -hydroxo complex as catalyst. Subsequent one-pot reduction afforded optically active β -fluoro- α -hy-

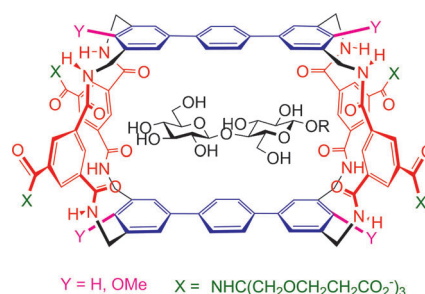
droxy esters. These compounds were then converted into β -fluoro- α -amino esters, which are potentially useful in medicinal chemistry research.

Carbohydrate Recognition

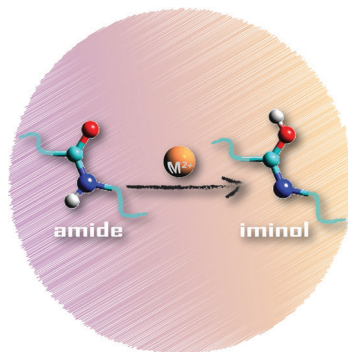
B. Sookcharoenpinyo, E. Klein, Y. Ferrand,
D. B. Walker, P. R. Brotherhood, C. Ke,
M. P. Crump, A. P. Davis* — 4586–4590

High-Affinity Disaccharide Binding by Tricyclic Synthetic Lectins

Stay flexible: Rigid preorganization is not always the best approach to molecular recognition. Unlike previous synthetic lectins, new receptors (see picture) were synthesized that possess conformational freedom which allows hydrophobically driven collapse of the cavity. Nonetheless, they bind their carbohydrate targets in water with ground-breaking affinities (up to 4500 M⁻¹ for methyl cellobioside, R = Me) and selectivities.



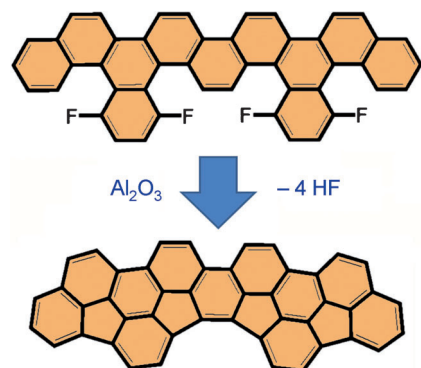
Rearranged: The attachment of gas-phase divalent metal ions that bind as strongly as Mg^{2+} and transition-metal ions to the dipeptide PhePhe results in displacement of the amide proton by the newly characterized iminol tautomerization rearrangement. More weakly coordinating ions bind in the known charge-solvation mode. Infrared multiple-photon dissociation spectroscopy using the free-electron laser clearly shows the tautomeric transition.



Peptide Conformations

R. C. Dunbar,* J. D. Steill, N. C. Polfer, G. Berden, J. Oomens — 4591 – 4593

Peptide Bond Tautomerization Induced by Divalent Metal Ions: Characterization of the Iminol Configuration



Building bowls: An effective intramolecular aryl–aryl coupling is the key step in rational fullerene synthesis and in synthesis of extended buckybowl structures. Such a process can be embodied very efficiently through quantitative HF elimination on active Al_2O_3 . The process is characterized by an unprecedentedly high chemoselectivity and regioselectivity.

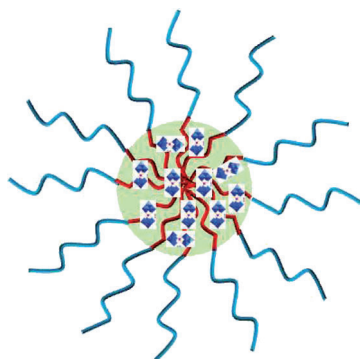
Aryl–Aryl Coupling

K. Y. Amsharov,* M. A. Kabdulov, M. Jansen — 4594 – 4597

Facile Bucky-Bowl Synthesis by Regiospecific Cove-Region Closure by HF Elimination



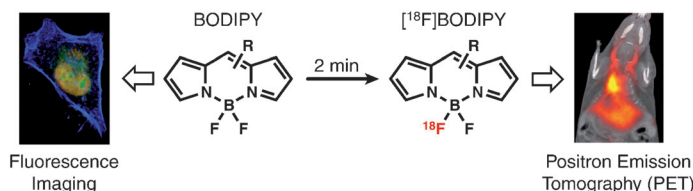
Core–shell nanostructures of a photoluminescent Eu-containing polyoxometalate (Eu-POM) with double-hydrophilic neutral–cationic block copolymer $\text{PEO}_{114}\text{-}b\text{-PDMAEMA}_{16}$ in aqueous solution were fabricated by self-assembly driven by electrostatic interactions (see scheme; neutral block blue, cationic block red). The emission of Eu-POM, which depends on the charge ratio of the Eu-POM/copolymer system, is enhanced up to 20-fold by complexation with the cationic PDMAEMA block.



Polyoxometalates

J. Zhang,* Y. Liu, Y. Li, H. X. Zhao, X. H. Wan* — 4598 – 4602

Hybrid Assemblies of Eu-Containing Polyoxometalates and Hydrophilic Block Copolymers with Enhanced Emission in Aqueous Solution



The best of both worlds: BODIPY-based imaging probes can be tracelessly transformed into hybrid PET/fluorescence imaging reagents by direct $^{19}\text{F}/^{18}\text{F}$ exchange without the need for redesign.

This approach has the potential to accelerate not only the development of imaging agents, but perhaps also the screening of therapeutic molecules.

Radiopharmaceuticals

J. A. Hendricks, E. J. Keliher, D. Wan, S. A. Hilderbrand, R. Weissleder,* R. Mazitschek* — 4603 – 4606

Synthesis of ^{18}F BODIPY: Bifunctional Reporter for Hybrid Optical/Positron Emission Tomography Imaging

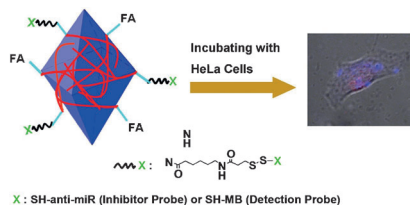


MicroRNA Detection

H. Dong, J. Lei, H. Ju,* F. Zhi, H. Wang,
W. Guo, Z. Zhu, F. Yan* — 4607–4612



Target-Cell-Specific Delivery, Imaging, and
Detection of Intracellular MicroRNA with
a Multifunctional SnO₂ Nanoprobe



Right on target: A multifunctional nanoprobe is designed for target-cell-specific imaging and in situ detection of intracellular miRNA. The nanoprobe is prepared by functionalizing SnO₂ nanoparticles with both folic acid (FA), a target-cell-specific moiety to recognize folate receptors overexpressed on cancer cells, and a gene probe to inhibit or recognize intracellular miRNA levels (see scheme).

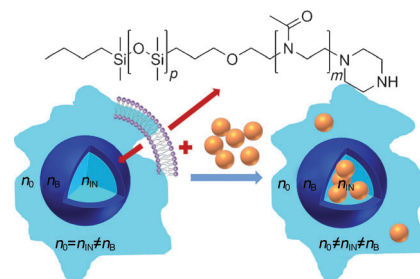
Nanoparticles

K. Jaskiewicz, A. Larsen, I. Lieberwirth,
K. Koynov, W. Meier, G. Fytas, A. Kroeger,*
K. Landfester — 4613–4617



Probing Bioinspired Transport of
Nanoparticles into Polymersomes

Transmembrane transport: A combination of photon and fluorescence correlation spectroscopies is used to study the internalization of nanoparticles into a minimal model system based on poly(dimethylsiloxane)-*block*-poly(2-methyloxazoline) vesicles (see picture). These techniques provide information about the kinetics and dynamics of this transport process in real time.



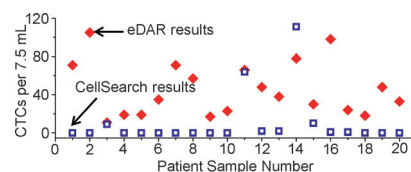
Tumor Cells

P. G. Schiro, M. Zhao, J. S. Kuo,
K. M. Koehler, D. E. Sabath,
D. T. Chiu* — 4618–4622



Sensitive and High-Throughput Isolation
of Rare Cells from Peripheral Blood with
Ensemble-Decision Aliquot Ranking

Enrichment of cells: An approach called ensemble-decision aliquot ranking (eDAR) for isolating rare cells from peripheral blood is described. The eDAR process has a recovery of over 93 % (number of runs $n=9$) with a zero false positive rate ($n=8$) and provides direct easy access to individual isolated live cells for downstream single-cell manipulation and analysis (CTCs = circulating tumor cells).



Back Cover

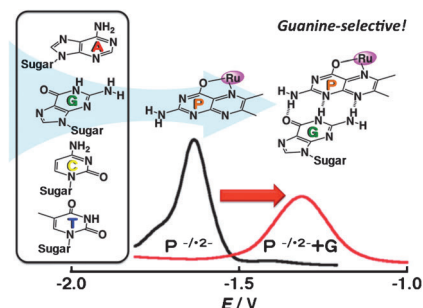
Cofactors

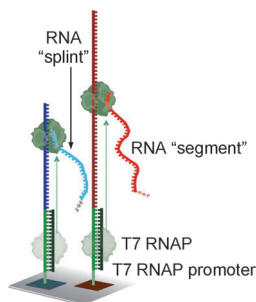
Y. Inui, S. Miyazaki, K. Ohkubo,
S. Fukuzumi,* T. Kojima* — 4623–4627



Regulation of Redox Potential of a Pterin
Derivative Bound to a Ruthenium(II)
Complex by Intermolecular Hydrogen
Bonding with Nucleobases

Potential control: A Ru^{II}-bound pterin forms a stable hydrogen-bonding adduct with a guanine derivative through three-point recognition. A large positive shift of the reduction potential of the pterin ligand up to +320 mV is observed (see picture). For the thymine derivative, the mode of hydrogen bonding is altered. Regulation of redox potentials of a pterin coenzyme by noncovalent interaction is demonstrated.



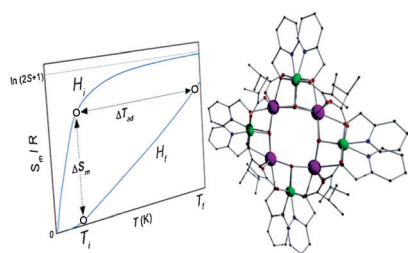


Gene Genie: RNA-mediated gene assembly is possible in a single day from oligonucleotide sequences on a DNA array. A T7 promoter is appended to each surface-bound oligonucleotide and many RNA copies of each are then produced with T7 RNA polymerase (see Figure). These RNA molecules self-assemble into the desired full-length transcript by hybridization and ligation, which is then converted into double-stranded DNA by reverse transcriptase polymerase chain reaction.

Gene Synthesis

C.-H. Wu, M. R. Lockett,
L. M. Smith* 4628–4632

RNA-Mediated Gene Assembly from
DNA Arrays

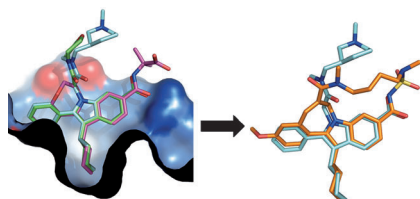


Playing it cool: Almost all of the constituent parts of the complex $[\text{Ln}^{\text{III}}_4\text{M}^{\text{II}}_8(\text{OH})_8(\text{L})_8(\text{O}_2\text{CR})_8]\text{X}_4$, namely the lanthanide ions Ln^{3+} , the transition-metal ions M^{2+} , the bridging ligand L, the carboxylates, and the counterions X can be exchanged, thus allowing a thorough understanding of the individual contributions to the magnetocaloric effect. Example in picture: Gd purple, Cu green, O red, N blue.

Cluster Compounds

T. N. Hooper, J. Schnack, S. Piligkos,*
M. Evangelisti,*
E. K. Brechin* 4633–4636

The Importance of Being Exchanged:
 $[\text{Gd}^{\text{III}}_4\text{M}^{\text{II}}_8(\text{OH})_8(\text{L})_8(\text{O}_2\text{CR})_8]^{4+}$ Clusters for
Magnetic Refrigeration

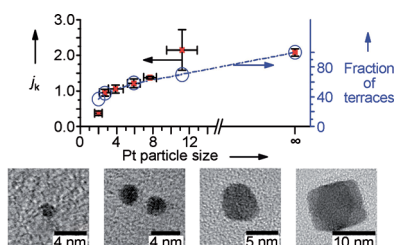


The concept of drug-likeness distills the physicochemical properties of small-molecule drugs to a set of rules. Macrocyclic drugs are known to break these rules. A structure-based macrocyclization strategy was applied to design new hepatitis C virus NS5B inhibitors with improved pharmacokinetic properties, exemplifying a rational strategy for overcoming the confines of standard “drug-like chemical space”.

Small-Molecule Inhibitors

M. D. Cummings,* T. Lin, L. Hu, A. Tahri,
D. McGowan, K. Amssoms, S. Last,
B. Devogelaere, M.-C. Rouan, L. Vijgen,
J. M. Berke, P. Dehertogh, E. Fransen,
E. Cleiren, L. van der Helm, G. Fanning,
K. Van Emelen, O. Nyanguile, K. Simmen,
P. Raboisson, S. Vendeville* 4637–4640

Structure-Based Macrocyclization Yields
Hepatitis C Virus NS5B Inhibitors with
Improved Binding Affinities and
Pharmacokinetic Properties



A matter of size: The particle size effect on the activity of the oxygen reduction reaction of size-selected platinum clusters was studied. The ORR activity decreased with decreasing Pt nanoparticle size, corresponding to a decrease in the fraction of terraces on the surfaces of the Pt nanoparticles (j_k = kinetic current density, see picture).

Oxygen Reduction Reaction

F. J. Perez-Alonso, D. N. McCarthy,
A. Nierhoff, P. Hernandez-Fernandez,
C. Strebel, I. E. L. Stephens, J. H. Nielsen,
I. Chorkendorff* 4641–4643

The Effect of Size on the Oxygen
Electroreduction Activity of Mass-Selected
Platinum Nanoparticles



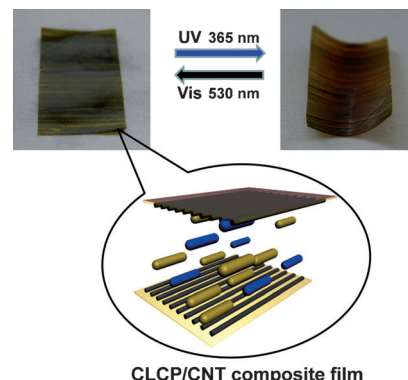
Liquid-Crystalline Polymers

W. Wang, X. Sun, W. Wu, H. Peng,*
Y. Yu* ————— 4644–4647



Photoinduced Deformation of Crosslinked Liquid-Crystalline Polymer Film Oriented by a Highly Aligned Carbon Nanotube Sheet

Bending over backwards: A highly aligned carbon nanotube sheet orients cross-linked liquid-crystalline polymer through a simple melting process (see picture). The resulting composite film can be rapidly bent and unbent by alternate irradiation with UV and visible light. The film also exhibits excellent mechanical and electrical properties due to the incorporation of aligned CNTs.



CLCP/CNT composite film

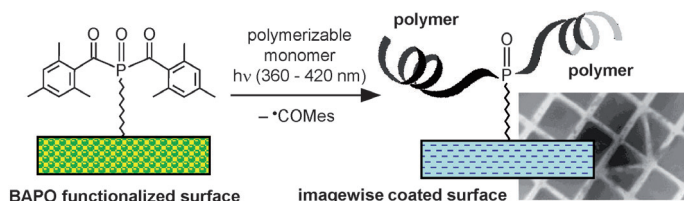


Photoinitiator Synthesis

A. Huber, A. Kuschel, T. Ott,
G. Santiso-Quinones, D. Stein, J. Bräuer,
R. Kissner, F. Krumeich, H. Schönberg,
J. Levalois-Grützmaker,
H. Grützmaker* ————— 4648–4652



Phosphorous-Functionalized Bis(acyl)phosphane Oxides for Surface Modification



Got a light? An efficient method for the synthesis of phosphorus-functionalized bis(acyl)phosphaneoxides (BAPOs) was developed, which allows the preparation of photoactive polymers or grafting of

these photoinitiators to various surfaces. Irradiation in the presence of polymerizable monomers leads to coatings that can be deposited imagewise.

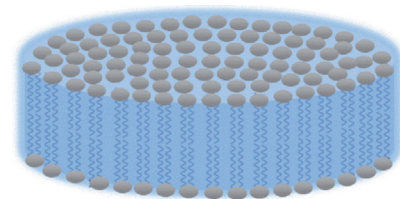
Polymer–Lipid Complexes

M. C. Orwick, P. J. Judge, J. Procek,
L. Lindholm, A. Graziadei, A. Engel,
G. Gröbner, A. Watts* ————— 4653–4657



Detergent-Free Formation and Physicochemical Characterization of Nanosized Lipid–Polymer Complexes: Lipodisq

Lipodisq particles are polymer–lipid complexes formed by detergent-free methods. Lipodisq particles containing dimyristoylphosphatidylcholine (DMPC) are characterized by increased lipid ordering compared to a DMPC dispersion. The styrene and maleic acid groups of the polymer interact with the DMPC lipid chains in bilayers, as well as lipid headgroups in the Lipodisq periphery (see picture).

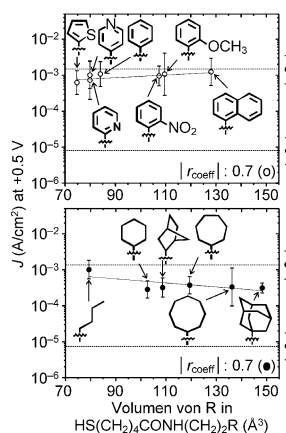


Self-Assembled Monolayers

H. J. Yoon, N. D. Shapiro, K. M. Park,
M. M. Thuo, S. Soh,
G. M. Whitesides* ————— 4658–4661

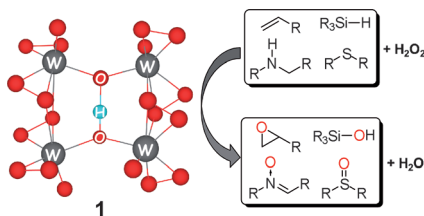


The Rate of Charge Tunneling through Self-Assembled Monolayers Is Insensitive to Many Functional Group Substitutions



Insensitivity: A series of molecules containing a common head group and body as well as structurally varied tail groups (-R) has been used in junctions with the structure $\text{Ag}/\text{S}(\text{CH}_2)_4\text{CONH}(\text{CH}_2)_2\text{R}/\text{Ga}_2\text{O}_3/\text{EGaIn}$ to study the rates of charge transport by tunneling. Changing the structure of R over a range of common aliphatic, aromatic, and heteroaromatic organic groups was found to not significantly influence the rate of tunneling (see plots; the dashed lines represent calibration standards).

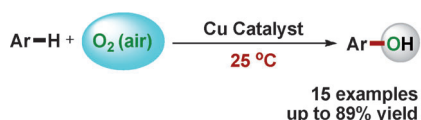
Acid assists: The reaction of $[\{WO(O_2)_2\}_2(\mu-O)]^{2-}$ with 0.5 equivalents of HNO_3 gave a tetranuclear peroxotungstate (**1**; see picture) that has a dramatically enhanced activity for the epoxidation of cyclooctene with H_2O_2 compared to various peroxotungstates. The **1**-catalyzed system was applicable to the selective oxidation of various kinds of substrates with 1.0–1.5 equivalents of H_2O_2 .



Homogeneous Catalysis

R. Ishimoto, K. Kamata,
N. Mizuno* _____ **4662–4665**

A Highly Active Protonated Tetranuclear Peroxotungstate for Oxidation with Hydrogen Peroxide

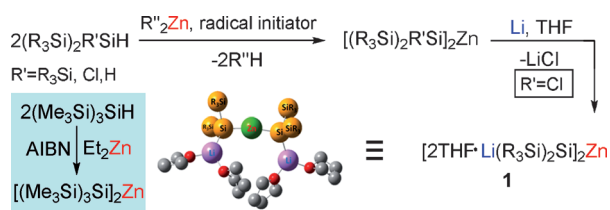


No pressure: The oxidation of aromatic C–H bonds at room temperature was realized through a copper-catalyzed “oxygenase-type” oxidation of arenes and heteroarenes in the presence of air (see scheme). The reaction involves an oxygen-atom transfer from O_2 in the air onto the substrates.

Aerobic Oxidation

Q. Liu, P. Wu, Y. Yang, Z. Zeng, J. Liu,
H. Yi, A. Lei* _____ **4666–4670**

Room-Temperature Copper-Catalyzed Oxidation of Electron-Deficient Arenes and Heteroarenes Using Air



Si–H bonds can be activated by organozinc and silylzinc compounds in the presence of minute amounts of radical initiators such as tBu_2Hg or AIBN, yielding zincosilanes in good yields (see

scheme). Activation of dihydrosilanes leads to geminal dizincosilanes. Zincio-bridged disilyllithium compounds, which have three (**1**) and four metal–silicon bonds, were also synthesized.

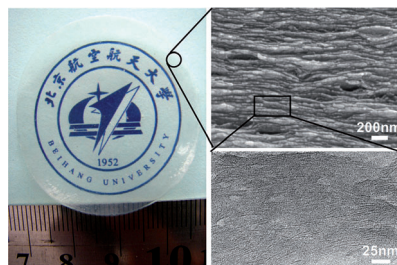
Si–H Bond Activation

R. Dobrovetsky, Y. Kratish, B. Tumanskii,
M. Botoshansky,
D. Bravo-Zhivotovskii,*
Y. Apeloig* _____ **4671–4675**

Radical Activation of Si–H Bonds by Organozinc and Silylzinc Reagents: Synthesis of Geminal Dizincosilanes and Zinciolithosilanes



Inspired by nacre, a layered poly(*N*-isopropylacrylamide)–clay nanocomposite hydrogel was successfully fabricated by combination of vacuum-filtration self-assembly and photo-initiated in situ polymerization. This bio-inspired layered nanocomposite hydrogel shows excellent mechanical properties, which can rival some biological soft tissues (see picture).



Bio-Inspired Hydrogels

J. F. Wang, L. Lin, Q. F. Cheng,*
L. Jiang _____ **4676–4680**

A Strong Bio-Inspired Layered PNIPAM–Clay Nanocomposite Hydrogel

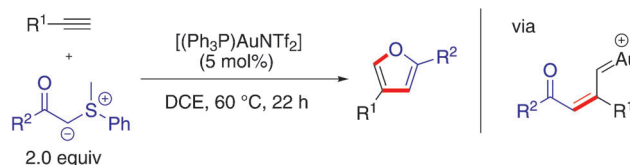


Inside Cover



Gold Catalysis

S. Kramer, T. Skrydstrup* — 4681–4684



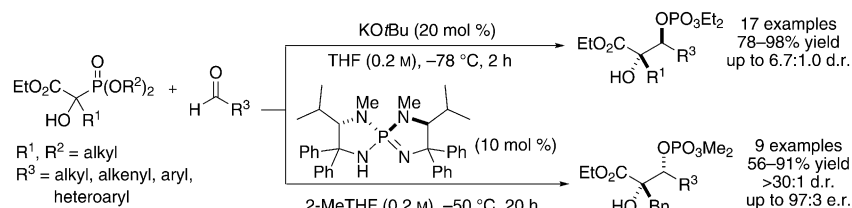
Gold-Catalyzed Carbene Transfer to Alkynes: Access to 2,4-Disubstituted Furans

Furans of gold: The first example of a gold-catalyzed intermolecular addition of carbon ylides to terminal alkynes is reported (see scheme; DCE = dichloroethane, Tf = trifluoromethanesulfonyl).

Subsequent intramolecular trapping of the generated gold carbene completes a formal [3+2] cycloaddition, which represents a novel synthesis of 2,4-disubstituted furans.

Direct Aldol Reaction

M. T. Corbett, D. Uraguchi, T. Ooi,*
J. S. Johnson* — 4685–4689



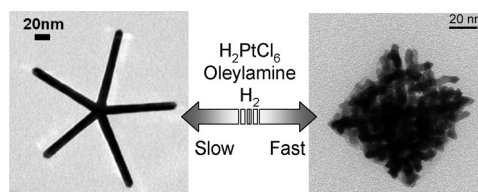
Base-Catalyzed Direct Aldolization of α -Alkyl- α -Hydroxy Trialkyl Phosphonoacetates

Pass the P: Catalytic direct aldol addition of α -hydroxy trialkyl phosphonacetates to aldehydes affords α -hydroxy- β -phosphonyloxy ester products (see scheme). The fully substituted glycolate enolate intermediate is generated in situ under mild

conditions by a [1,2] phosphonate–phosphate rearrangement. High enantioselectivity and dramatic enhancement of reaction diastereocontrol is realized by the application of chiral iminophosphorane catalysts.

Nanostructures

L.-M. Lacroix,* C. Gatel, R. Arenal,
C. Garcia, S. Lachaize, T. Blon,
B. Warot-Fonrose, E. Snoeck, B. Chaudret,
G. Viau — 4690–4694



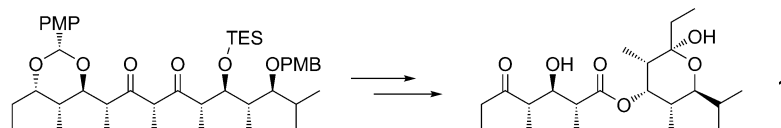
Tuning Complex Shapes in Platinum Nanoparticles: From Cubic Dendrites to Fivefold Stars

A platinum star performance: Quasi-single-crystalline Pt nanoparticles with peculiar morphologies—cubic dendrites, planar tripods, and fivefold stars—were

synthesized in high yield. Shape selectivity was achieved by finely tuning the growth kinetics under a dihydrogen atmosphere.

Biomimetic Synthesis

R. H. Currie,
J. M. Goodman* — 4695–4697

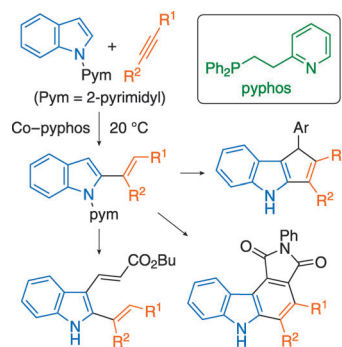


In Silico Inspired Total Synthesis of (–)-Dolabriferol

Going retro: The diazabicycloundecane-induced retro-Claisen rearrangement of a linear precursor serves as the key step to form the hindered ester of the polypropionate dolabriferol (**1**, see scheme,

PMB = *p*-methoxybenzyl, PMP = *p*-methoxyphenyl, TES = triethylsilyl). The rearrangement is thought to mimic the biosynthetic formation of **1**.

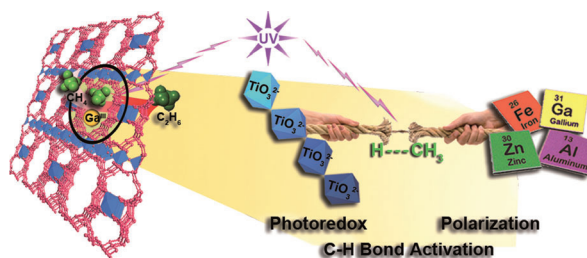
Direct alkenylation of the C2-position of indoles bearing an easily removable N-pyrimidyl group with alkynes has been achieved by using a cobalt catalyst complexed with a phosphine–pyridine bidentate ligand. This reaction has wide substrate scope and is highly efficient and stereoselective at room temperature. The alkenylated indoles serve as useful platforms for further synthetic transformations (some products of these transformations are shown in the scheme).



C–H Bond Functionalization

Z. Ding, N. Yoshikai* — 4698 – 4701

Mild and Efficient C2-Alkenylation of Indoles with Alkynes Catalyzed by a Cobalt Complex



Breaking down methane: A Ga³⁺-modified microporous titanosilicate (ETS-10) exhibits distinct photoactivity for the cleavage of the methane C–H bond at room temperature. The highly enhanced

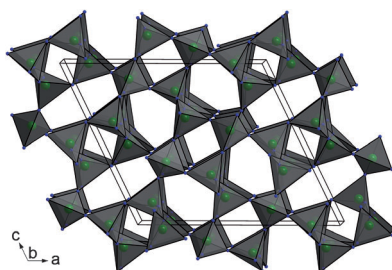
activity is attributed to the synergistic effect of gallium-induced C–H bond polarization and a titania-based photoredox process.

C–H Bond Activation

L. Li, Y. Y. Cai, G. D. Li, X. Y. Mu, K. X. Wang, J.-S. Chen* — 4702 – 4706

Synergistic Effect on the Photoactivation of the Methane C–H Bond over Ga³⁺-Modified ETS-10

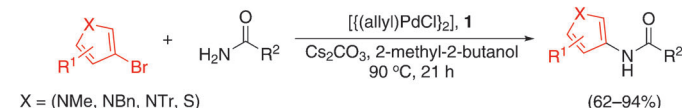
Restructuring: An unprecedented framework structure made up of tetrahedra has been discovered in a novel high-pressure polymorph of the phosphorus oxonitride PON by treating a single-source precursor at 12 GPa and 1250 °C. It is the first polymorph of PON that does not crystallize in a structure type known from SiO₂.



Solid-State Structures

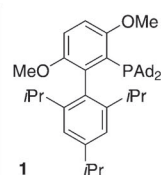
D. Baumann, S. J. Sedlmaier, W. Schnick* — 4707 – 4709

An Unprecedented AB₂ Tetrahedra Network Structure Type in a High-Pressure Phase of Phosphorus Oxonitride (PON)



The incredible bulk: The first palladium-catalyzed amidation of five-membered heterocyclic bromides with multiple heteroatoms was achieved using the Pd/1 catalyst system. N-Arylated imidazoles, pyrazoles, thiazoles, pyrroles, and thio-

phenes were synthesized in moderate to excellent yield. Experimental results and DFT calculations point to the need for an electron-rich and sterically demanding biaryl phosphine ligand to promote these difficult reactions.



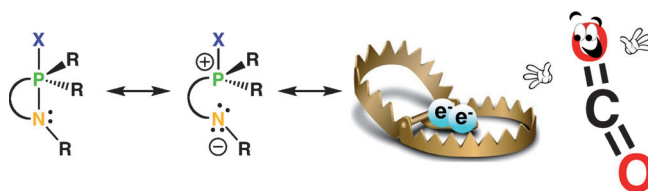
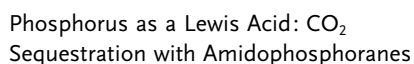
Cross-Coupling

M. Su, S. L. Buchwald* — 4710 – 4713

A Bulky Biaryl Phosphine Ligand Allows for Palladium-Catalyzed Amidation of Five-Membered Heterocycles as Electrophiles

Carbon Dioxide Capture

L. J. Hounjet, C. B. Caputo,
D. W. Stephan* _____ **4714–4717**

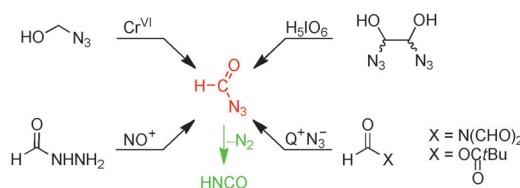
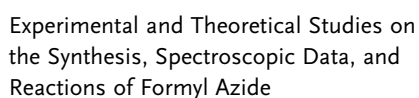


CO₂ snapper: Compounds containing both acidic and basic P,N functionalities have been prepared. Of these, two amidophosphoranes containing highly reactive P–N bonds within four-membered

rings react rapidly with CO₂, resulting in relief of ring strain. These compounds demonstrate the utility of phosphorus as a Lewis acid for small-molecule activation.

Acyl Azides

K. Banert,* C. Berndt, M. Hagedorn,
H. Liu, T. Anacker, J. Friedrich,*
G. Rauhut* **4718–4721**



Small is beautiful: spectroscopic proof or any other indication for the existence of formyl azide (HC(O)N_3) has until now been lacking. Although it liberates dini-

trogen much more rapidly than homologous acyl azides, it has been prepared for the first time by four different methods (see scheme).

DOI: 10.1002/anie.201202311

50 Years Ago ...

Angewandte Chemie International Edition was first published in 1962, the mother journal first in 1888. In this monthly flashback, we feature some of the articles that appeared 50 years ago. This look back can open our eyes, stimulate discussion, or even raise a smile.

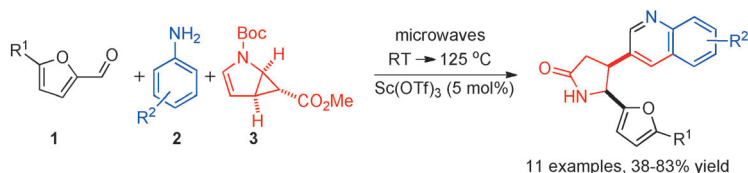
In the 1960s, mercurial diuretics—drugs that promote the formation of urine—were still the agents of choice if rapid action on the kidneys was required, however, given the toxicity of organo-mercury species, new orally active drugs were required. In a Review, E. Schlittler, G. Destevens, and L. Werner discussed the developments in non-mercurial diuretics, in particular the sulfonamide derivatives chlorothiazide and hydrochlorothiazide. In early 1961, hydrochlorothiazide was the leading product worldwide and the total sales for all non-mercurial diuretics in the USA was 45 million dollars—a large turnover in those days.

Drug synthesis was also reported by U. Schmidt and F. Geiger, who discussed the total synthesis of the antibiotics thiolutin, aureothricin, and holomycin in a Communication. These antibiotics contain condensed pyrrolonedithiol ring systems and are active against pathogenic fungi and Gram-negative and Gram-positive bacteria.

NMR spectroscopy was already beginning to have applications in physical chemistry, and W. Seiffert, H. Zimmermann, and G. Scheibe reported how the proton magnetic resonance spectra of aromatic heterocyclic compounds could be used for estimating π -electron den-

sities in the molecular ground state. This estimation was carried out by comparing the chemical shifts of the molecule in question with those of benzene, and calculating the electron densities from these shift differences by using a calibration curve. The method was applied to pyridine and the experimentally derived values were comparable to those derived from quantum mechanical calculations.

Read more in Issue 5/1962



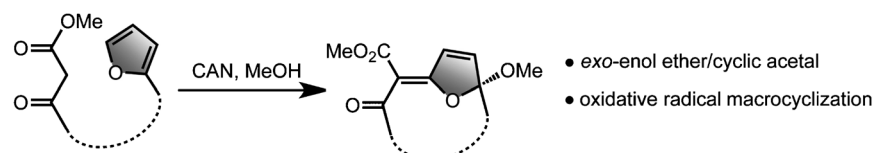
Ménage à trois: In a three-component reaction, furancarbaldehydes **1**, anilines **2**, and the monocyclopropanated pyrrole **3** can be assembled highly stereoselectively

to give *cis*-4,5-disubstituted pyrrolidinones (see scheme; Boc = *tert*-butoxycarbonyl). The products are lead structures for pharmaceutically important compounds.

Multicomponent Reactions

S. Roy, O. Reiser* — 4722–4725

A Catalytic Multicomponent Approach for the Stereoselective Synthesis of *cis*-4,5-Disubstituted Pyrrolidinones and Tetrahydro-3*H*-pyrrolo[3,2-*c*]quinolines



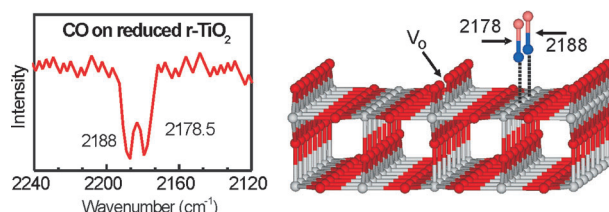
It's all in the CAN: Cerium ammonium nitrate (CAN) promotes the oxidative radical cyclization of furan β-ketoesters to form macrocycles of varying ring sizes.

The reaction is tolerant of unsaturation, oxygenation, and nitrogen and oxygen heterocycles in the carbon backbone tether.

Synthetic Methods

K. C. Nicolaou,* C. R. H. Hale, C. Ebner, C. Nilewski, C. F. Ahles, D. Rhoades — 4726–4730

Synthesis of Macrocyclic Heterocycles through Intramolecular Oxidative Coupling of Furanoid β-Ketoesters



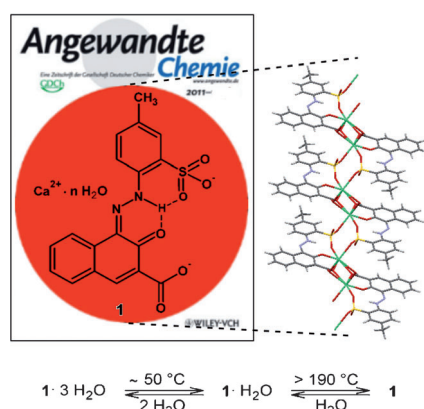
Chemistry at defects: The concentration of defect sites at rutile TiO₂ (r-TiO₂) surfaces of both single crystals and powder particles was determined by UHV-FTIR spectroscopy using CO as a probe

molecule (see picture). The potential of this novel approach is demonstrated by unraveling the mechanism of reductive coupling of formaldehyde to give ethylene.

Surface Chemistry

M. Xu, H. Noei, K. Fink, M. Muhler, Y. Wang,* C. Wöll* — 4731–4734

The Surface Science Approach for Understanding Reactions on Oxide Powders: The Importance of IR Spectroscopy



The Red carrying the news around the world: Most newspapers and journals worldwide (including *Angewandte Chemie*) are printed with Pigment Red 57:1. The crystal structures of this pigment in various hydration states have now been determined by X-ray powder diffraction.

Organic Pigments

S. L. Bekö, S. M. Hammer, M. U. Schmidt* — 4735–4738

Crystal Structures of the Hydration States of Pigment Red 57:1

Inside Back Cover

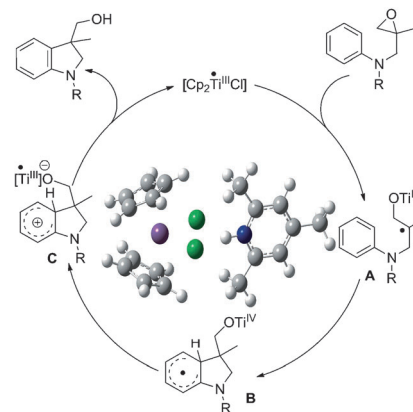
Radical Chemistry

A. Gansäuer,* M. Behlendorf,
D. von Laufenberg, A. Fleckhaus, C. Kube,
D. V. Sadasivam,
R. A. Flowers, II* ——— 4739–4742



Catalytic, Atom-Economical Radical
Arylation of Epoxides

A slow electron waltz: Catalysis in single-electron steps with radicals as intermediates is essential for an atom-economical arylation of epoxides with a proton-coupled electron transfer as a key step. Stabilization of the catalyst is essential for low catalyst loading, as demonstrated by reaction-progress kinetic analysis, cyclic voltammetry, and calculations.



Electroless Deposition

N. Kränzlin, S. Ellenbroek,
D. Durán-Martín,
M. Niederberger* ——— 4743–4746



Liquid-Phase Deposition of Freestanding
Copper Foils and Supported Copper Thin
Films and Their Structuring into
Conducting Line Patterns



Metal foils: A simple electroless liquid-phase deposition technique gives access to freestanding copper foils and supported copper thin films. The films can be

easily structured into conducting line patterns for electronics applications (see picture).

Front Cover



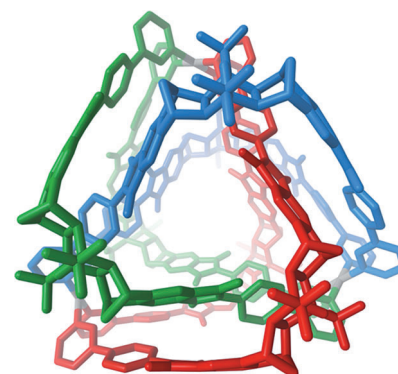
Knot Structures

D. M. Engelhard, S. Freye, K. Grohe,
M. John, G. H. Clever* ——— 4747–4750



NMR-Based Structure Determination of
an Intertwined Coordination Cage
Resembling a Double Trefoil Knot

A knot that ties itself! The entanglement of six ligands coordinated to three Pd^{II} ions results in the quantitative formation of a walnut-shaped supramolecular cage. Each of the two hemispheres resembles a trefoil knot. The solution-state structure was elucidated using a combination of NMR experiments and calculated model structures. The final structure was selected from several models by topological analyses and encapsulation of chiral camphorsulfonate ions.



Supporting information is available
on www.angewandte.org
(see article for access details).



A video clip is available as Supporting
Information on www.angewandte.org
(see article for access details).



This article is available
online free of charge
(Open Access).



This article is accompanied by a cover picture (front or back cover, and inside or outside).

Sources

Product and Company Directory

You can start the entry for your company in "Sources" in any issue of *Angewandte Chemie*.

If you would like more information, please do not hesitate to contact us.

Wiley-VCH Verlag – Advertising Department

Tel.: ☎ 62 01 - 60 65 65

Fax: ☎ 62 01 - 60 65 50

E-Mail: MSchulz@wiley-vch.de

Service

Spotlight on Angewandte's

Sister Journals _____ 4514–4516

Preview _____ 4752

Angewandte Corrigendum

In this communication, the interpretation of ESI-MS data, obtained at low resolution, was misled. On page 11 448, the section around Figure 1 thus should read as follows:

"An ESI-MS analysis at low resolution (in the positive mode) for a 1:1 mixture of benzamide **1** and AuCl₃ in CD₃CN at room temperature (immediately after mixing) showed intensive peaks at *m/z* 548 and 550 (Figure 1), which may be attributed to the divinylgold species **9** and its ³⁷Cl derivative, respectively.

Figure 1. Divinylgold species **9** suggested but not confirmed by low resolution ESI-MS. In the negative ESI-MS mode at low resolution, the cluster peaks observed at *m/z* 460 and 462 were attributed to **A** (C₁₀H₈AuCl₃NO, exact mass 459.93) and its ³⁷Cl derivative. Both data sets also suggested the formation of the mono- and divinylgold species."

In the Supporting Information, page 17, the deuterium in the chemical structures suggested for the peaks at *m/z* 461 and 463 (lower spectrum) should be replaced with hydrogen, and the *m/z* 461 and 463 values should be counted as *m/z* 460 and 462, based on the fact that the reference peak AuCl₄[−] (*m/z* 336.8) appears at *m/z* 337.9. Accordingly, the peak at *m/z* 502.0 attributed to **A**(CH₃CN) should be counted as 501.0. Also, the assignment of Au-**1** for the peak at *m/z* 520 should be replaced by "unknown structure".

The ESI-MS data were obtained for the samples prepared in CD₃CN, as in the case of the NMR analysis samples. The ESI-MS analyses were carried out within 10 min of the sample preparation. Before injecting the sample, the turbospray was washed with CH₃CN carefully; hence, residual CH₃CN can be mixed with the sample solution. However, due to the low resolution and a calibration error, numeric errors in the ESI-MS mass were observed, as noted for the reference peak AuCl₄[−].

Characterization of Vinylgold Intermediates: Gold-Mediated Cyclization of Acetylenic Amides

O. A. Egorova, H. Seo, Y. Kim, D. Moon, Y. M. Rhee, K. H. Ahn* — 11446–11450

Angew. Chem. Int. Ed. **2011**, 50

DOI: 10.1002/anie.201106132